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URANIUM AGE DETERMINATION BY MEASURING THE ^{230}Th / ^{234}U RATIO

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A radiochemical isotope dilution mass spectrometry method has been developed to determine the age of uranium materials. The amount of ^{230}Th activity, the first progeny of ^{234}U, that had grown into a small uranium metal sample was used to determine the elapsed time since the material was last radiochemically purified. To preserve the sample, only a small amount of oxidized uranium was removed from the surface of the sample and dissolved. Aliquots of the dissolved sample were spiked with ^{233}U tracer and radiochemically purified by anion-exchange chromatography. The ^{234}U isotopic concentration was then determined by thermal ionization mass spectrometry (TIMS). Additional aliquots of the sample were spiked with ^{229}Th tracer, and the thorium was purified using two sequential anion-exchange chromatography separations. The isotopic concentrations of ^{230}Th and ^{232}Th were determined by TIMS. The lack of any ^{232}Th confirmed the assumption that all thorium was removed from the uranium sample at the time of purification. The ^{230}Th and ^{234}U mass concentrations were converted to activities and the $^{230}Th/^{234}U$ ratio for the sample was calculated. The experimental $^{230}Th/^{234}U$ ratio showed the uranium in this sample was radiochemically purified in about 1945.

Introduction

Numerous radiochronology methods have been developed that rely on determining the disequilibrium in uranium series radionuclides (Figure 1). Most of these are used to study geologic processes, and take advantage of the long half-life of ^{230}Th, which, if removed from uranium by a chemical process takes approximately 5 x 10^5 years to regain secular equilibrium with its parent, ^{234}U. Examples include dating of carnotite minerals[1], Fe-Mn deposits[2], and travertine carbonate formations[3].

The ingrowth of ^{230}Th can also be used to determine the time elapsed since a source of uranium was last radiochemically purified. However, uranium extraction from ores has only been occurring for just over 100 years, and the amount ^{230}Th that has grown into purified uranium is very small compared to geologic samples. To effectively determine the ^{230}Th that has grown into a sample of uranium, either the Th has to be separated from a very large sample of uranium, or extremely sensitive analytical methods have to be used. In both cases, extensive radiochemistry is required to purify the ^{230}Th prior to analysis to remove interfering species. The ^{230}Th / ^{234}U ratio has been used to determine the age of highly enriched uranium using isotope dilution thermal ionization mass spectrometry (ID-TIMS), isotope dilution alpha spectrometry (ID-AS), and inductively coupled plasma mass spectrometry (ICP-MS).[4] However, the authors concluded that approximately 10 mg of HEU and 1 g of natural U would be required to determine the age using ID-TIMS or ID-AS, and that ICP-MS could only determine the age of enriched uranium containing at least 0.01 % ^{234}U by weight.[4] These limitations would make this method only marginally useful for nuclear forensic applications, where much smaller quantities of uranium are sometimes all that is available.

The Nonproliferation Technology Section, at the Savannah River Technology Center received a request to determine the age of a small piece of uranium metal. Because the material was at least a year old, the ^{230}Th ingrowth, while very small, was the logical isotope in the U series that could be measured to determine its age. Radiochemical isotope dilution thermal ionization mass spectrometry (TIMS) methods were used by NTS to determine the uranium isotopic composition of the sample and measure ^{230}Th activity in the sample to estimate the year the uranium was manufactured. This method is capable of determining the age of 100 μg samples of 50 year old natural uranium.

Experimental

Sample Preparation

The sample provided was a small uranium metal cylinder approximately 0.8 cm diameter and 2 cm long. A thin layer of oxidation had formed on the surface. Some of the oxidized uranium had been transferred to the inside of the bag the sample was stored in, and served as a convenient method by which to obtain a small amount of the uranium, while maintaining the integrity of the bulk sample.

To collect a subsample the uranium, the sample was transferred to a clean bag, and an approximately one inch square of the original bag containing most of the oxidized material was leached in 25 mL of 8 M HNO_3 to dissolve the uranium dust. After 2 hours the bag was removed from the solution and rinsed with 8 M HNO_3 adding the rinse to the leach solution. The leach solution was transferred to a 100 mL Class A volumetric flask and brought up to volume with 8 M HNO_3 (Solution 1). Two successive 1:100 dilutions of Solution 1 were made, labeled Solution 2 and Solution 3, to produce a uranium concentration in the appropriate range for analysis by mass spectrometry.

Uranium Purification

Three 1.00 mL aliquots of Solution 3 were pipetted into 5 mL conical Teflon™ vials. One aliquot was set aside for direct analysis by thermal ionization mass spectrometry. Of the remaining two aliquots, one was spiked with ^{233}U as a radiochemical yield tracer. A blank sample and QC sample of natural uranium (both spiked with ^{233}U tracer) were prepared to run through the radiochemical separation with the two sample aliquots. The samples, blank, and QC were taken to dryness on a hotplate and redissolved in 3.00 mL of 9 M HCl to prepare them for the anion exchange chromatography separation.

Anion exchange columns containing 0.50 mL of 100 - 200 mesh AG1x4 Cl^- form resin were used for the purification of the uranium samples. The columns were prepared by passing 5 mL of 0.1 M HCl through each column to eliminate any uranium background from the resin, followed by 5 mL of 9 M HCl to condition the column for the samples. The samples were then passed through the columns, and the vials rinsed twice with 1 mL of 9 M HCl, adding the rinse to the columns. The columns were then rinsed with an additional 2.5 mL of 9M HCl followed by 1.25 mL of 8 M HNO_3 to remove any iron present. Finally, the uranium was eluted into 5 mL conical Teflon™ vials with an additional 4 mL of 8 M HNO_3 and submitted for isotopic uranium determination by TIMS.

Thorium Purification

Three 20.0 mL aliquots of Solution 1 were pipetted into 50 mL Pyrex™ beakers. Two aliquots were spiked with ^{229}Th as a radiochemical yield tracer. A reagent blank was also prepared by spiking 20.0 mL of 8 M HNO_3 (the matrix of Solution 1) with ^{229}Th tracer. An aliquot of ^{229}Th tracer was also submitted directly for isotopic analysis by mass spectrometry to determine any ^{232}Th and ^{230}Th isotopic impurities. The two spiked aliquots of Solution 1, the unspiked aliquot of Solution 1, and the spiked reagent blank were all taken to dryness on a hotplate and redissolved in 25 mL of 8 M HNO_3.

The thorium was separated from the uranium using a 10 mL column anion exchange column followed by a 0.5 mL anion exchange column in order to get sufficient decontamination from uranium. The first columns were prepared by adding 10 mL 100 – 200 mesh AG1x8 Cl^- form resin to each of the four ion-exchange columns and rinsing them with 50 mL 0.1 M HCl to remove any trace thorium impurity in the resin. After converting the columns to the NO_3^- form by adding 50 mL 8 M HNO_3, the samples were added to the columns. The beakers were rinsed 3 times with 10 mL 8 M HNO_3 and added to the columns. The columns were then rinsed with an additional 45 mL 8 M HNO_3. Clean beakers were placed under the columns and the thorium was eluted with 60 mL of 9 M HCl. These solutions were taken to dryness on a hotplate, the residue was redissolved in 2 mL of 8 M HNO_3, and each sample was transferred to a 5 mL conical Teflon™ vial. The beakers were rinsed 2 times with 1 mL 8 M HNO_3, and the rinse solutions were added to their respective vials.

The second columns used for a final cleanup were 0.5 mL AG1x4 100 – 200 mesh anion exchange resin columns rinsed with 5 mL 0.1 M HCl, followed by conversion to NO_3^- with 5 mL 8 M HNO_3. The samples were then passed over the columns, and the vials rinsed 3 times with 1 mL of 8 M HNO_3, adding the rinse solutions to the columns. The columns were rinsed with an additional 2 mL of 8 M HNO_3, and the thorium was eluted into clean 5 mL conical Teflon™ vials with 5 mL of 9 M HCl. The samples were taken to dryness under a heatlamp, wet ashed with 1 mL 8 M HNO_3, and submitted for analysis by mass spectrometry.

Mass Spectrometry

The instrument used for this work is a Knolls Atomic Power Laboratory (KAPL) design three stage thermal ionization mass spectrometer. Samples were analyzed by sorbing the uranium or thorium onto ion exchange resin beads and mounting the beads onto rhenium filaments. The uranium and thorium were thermally vaporized and ionized, sorted by two 90° magnetic sectors and an electrostatic sector, and detected by single ion counting. The instrument has a dynamic range of about 10^9, but the detector limit is about 10^7. The normal uranium sample size is approximately 1 ng.

Each of the uranium samples was redissolved in 10 μl of 9 M HCl before the addition of two ion exchange resin beads (DOWEX AG 1-X2 conditioned in nitric acid). The thorium samples were redissolved in 8 M HNO_3 but were otherwise treated the same. The sample vials were stirred/gyrated overnight, and the beads were mounted to degassed "vee" type rhenium filaments using collodion thinned with methanol as adhesive.

The filaments were loaded into the three stage thermal ionization mass spectrometer and the source chamber evacuated. The beads were decomposed by heating the filament to about 1000°C while keeping the pressure below 3×10^{-7} torr, then allowed to cool for a minimum of 30 minutes before analysis. This process takes from 12 to 16 minutes and reduces the resin beads to small carbon rich chips containing the sample. Uranium filaments were reheated to about 1500°C for tuning and calibration using a 12 minute process. The thorium filaments were reheated to about 1550°C in a 16 minute process. The timed reheat sequences are to allow the chemistry/kinetics that occurs on the filaments to develop similarly for the entire set. The instrument was tuned and calibrated using normal uranium methods for all of the filaments due to the residual uranium in the thorium samples. The normal uranium calibration uses 2 points (masses 238 and 235) to account for the various offsets in the digital analog converter (DAC) and source high voltage supply. Mass spectra were made on each filament, and the calibration checked prior to raising the temperature to data collection levels.

Normal temperatures for data collection with uranium filaments range from 1550 to 1650°C. Higher temperatures will ionize more efficiently, but the sample uranium evaporates faster reducing the time available for data collection. Thorium filaments operate hotter than uranium filaments, at about 1700°C. After adjusting a thorium filament to a temperature for acceptable mass 232 signals, any residual uranium ion current lasted only a few minutes.

While collecting data, the controller steps the accelerating high voltage causing the instrument to switch from mass to mass, cyclically from high to low to high, counting pulses from the detector. A single cycle through the masses took about a minute. The filaments were counted for 30 – 60 minutes, and were typically not run to exhaustion. The resulting count data was scanned for outliers, and isotopic concentrations were calculated using standard methods for isotope dilution mass spectrometry. All sources of uncertainty were propagated in quadrature, and an uncertainty budget is shown in Table 1.

Results

The isotopic composition of the uranium in the unspiked sample, the spiked sample, and the QC sample are summarized in Table 2. Both the spiked sample and the QC sample were corrected for isotopic impurities in the ^{233}U tracer. The sample has a uranium isotopic composition similar to natural uranium, and the lack of detectable ^{236}U indicates that it was never irradiated in a nuclear reactor. Table 3 shows the concentration of ^{238}U determined in the spiked sample (Solution 3) and the QC sample. The concentration of uranium in Solution 3 was also used to calculate the concentration of uranium in the original sample, Solution 1.

Thorium isotopic impurities were determined in the ^{229}Th tracer so corrections could be applied when calculating the thorium isotopic concentrations in the samples and reagent blank. The ^{232}Th/^{229}Th ratio in the tracer was 19.987 and the ^{230}Th/^{229}Th ratio was 0.0017. Thorium isotopic concentrations determined in Solution 1 and the spiked reagent blank are shown in Table 4. Measurable ^{232}Th was found in the reagent blank, and was statistically equal to the ^{232}Th found in Solution 1. This indicates that when the uranium was purified, no significant thorium was present, a requirement for calculating the age of the material based on ^{230}Th growth.

The age of the uranium was calculated from the ingrowth ^{230}Th from the radioactive decay of ^{234}U, with the assumption that ^{234}U and ^{238}U were in secular equilibrium and that no ^{230}Th was present at the time the uranium metal was produced. The equation for calculating the ^{230}Th at a given time after the uranium was radiochemically purified is given in Figure 2, and is valid if no ^{230}Th was present immediately after purification, and the time elapsed since purification is less that 100 years.

A plot of the change in ^{230}Th / ^{234}U ratio as a function of time was generated using the equation shown in Figure 3 and includes the experimentally determined ^{230}Th / ^{234}U ratio showing the date of purification for the uranium. The ^{230}Th / ^{234}U activity ratios calculated using the data from the two ^{230}Th measurements and the ^{238}U measurement were $(5.13 \pm 0.67) \times 10^{-4}$ and $(5.23 \pm 0.67) \times 10^{-4}$, which correspond to production dates of 1946 ± 7 years and 1945 ± 7 years, respectively.

Conclusions

Isotope dilution thermal ionization mass spectrometry has sufficient sensitivity to determine the age of 100 μg size samples of uranium. This method could certainly be employed as a nuclear forensic method to determine the age of small quantities of uranium metal or salts. Accurate determination of the ultra-trace ^{230}Th radiochemically separated from the uranium is possible due to the use of ^{229}Th as an isotope dilution tracer. The precision in the experimental age of the uranium could be improved by making additional replicate measurements of the ^{230}Th / ^{234}U isotopic ratio or using a larger initial sample.

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Table 1: Uncertainty budget for uranium and thorium isotopic analyses. All sources of uncertainty were propagated in quadrature.

Source of Measurement Uncertainty	**Typical Contribution to Uncertainty in Measured U or Th Concentration**
^{233}U or ^{229}Th Concentration in Tracer	3 - 5 %
Isotopic Impurities in Tracer	0.1 – 3%
Sample Volume	1 - 2 %
Pipet Volume	2 %
Isotope Mass Bias in Mass Spectrometer	0.2 %
Background (Leakage Current)	0.01 - 1 %
Counting Statistics	0.01 – 15%
Overall Uncertainty in Measured U or Th Concentration	**4 – 16%**

Table 2: Uranium isotopic composition in samples. The bottom row shows the certified values for the QC sample, which are in good agreement with the experimentally determined values.

Sample Description	238 Atom %	236 Atom %	235 Atom %	234 Atom %
Unspiked Sample	99.26 ± 0.59	None Detected	0.732 ± 0.012	0.0062 ± 0.0003
Spiked Sample	99.27 ± 0.59	None Detected	0.724 ± 0.012	0.0056 ± 0.0019
QC Sample Measured	99.27 ± 0.35	None Detected	0.724 ± 0.007	0.0056 ± 0.0005
Natural Uranium and QC Certified Isotopic Composition	99.275	0	0.720	0.0055

Table 3: Uranium concentration in sample solutions and QC standard. The bottom row shows the certified values for the QC material, which are in good agreement with the measured value.

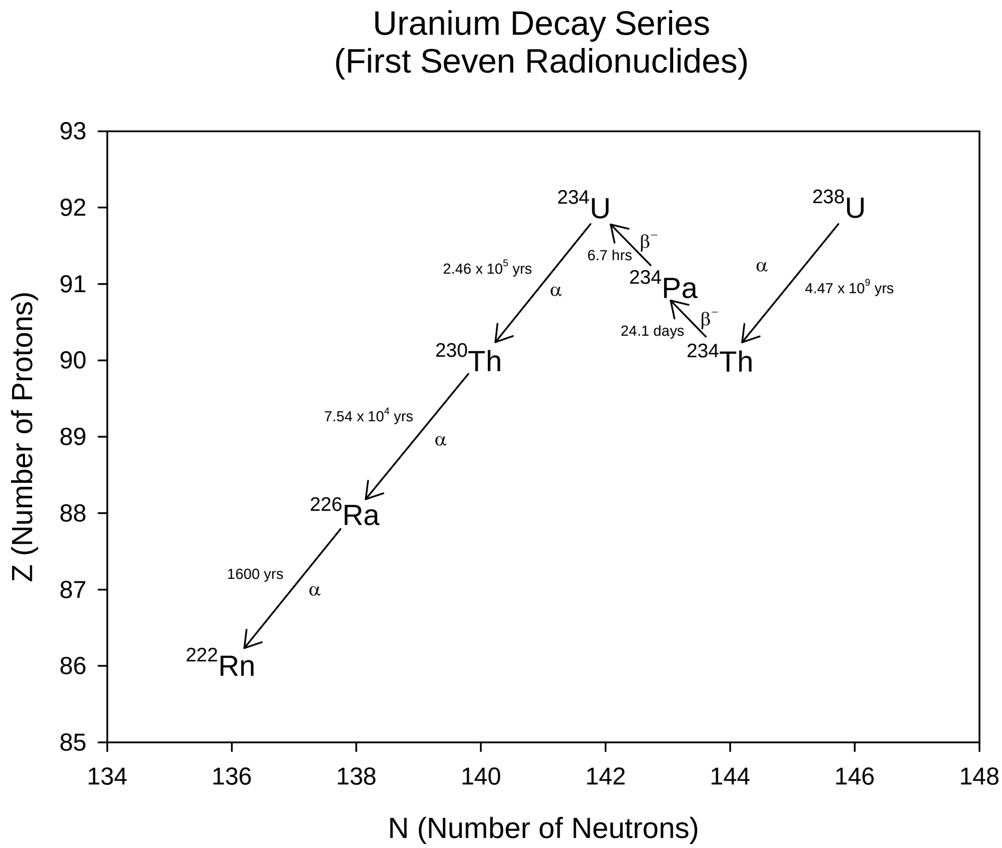
Sample Description	**^{238}U pg / mL**	**^{238}U pCi / mL**
Solution 1	$(5.50 \pm 0.17) \times 10^{6}$	1.85 ± 0.06
Solution 3	550.2 ± 9.8	$(1.85 \pm 0.03) \times 10^{-4}$
QC Measured	3261 ± 326	$(11.0 \pm 1.1) \times 10^{-4}$
QC Certified Value	2990 ± 290	$(10.0 \pm 1.0) \times 10^{-4}$

Table 4: Thorium isotopic concentrations in sample solution and reagent blank

Sample Description	^{230}Th pg / mL	^{232}Th pg / mL	^{230}Th pCi / mL	^{232}Th pCi / mL
Solution 1	0.0460 ± 0.0058	37.8 ± 4.4	(9.5 ± 1.2) x 10^{-4}	(4.16 ± 0.48) x 10^{-7}
Solution 1 (replicate)	0.0469 ± 0.0058	40.9 ± 4.6	(9.7 ± 1.2) x 10^{-4}	(4.50 ± 0.51) x 10^{-7}
Reagent Blank	< 0.0005	36.5 ± 4.8	< 1 x 10^{-5}	(4.02 ± 0.53) x 10^{-7}

S.P. LaMont, List of Figures:

S.P. LaMont, Figure 1



S.P. LaMont, Figure 2

$$A_{Th} = [\lambda_U \lambda_{Th} / (\lambda_{Th} - \lambda_U)] N^0_U (e^{-\lambda_U t} - e^{-\lambda_{Th} t})$$

Where:

A_{Th}	=	^{230}Th activity at time "t"
λ_U	=	Decay constant for ^{234}U
λ_{Th}	=	Decay constant for ^{230}Th
N^0_U	=	Number of ^{234}U atoms at time of separation
t	=	time elapsed after separation

S.P. LaMont, Figure 3